(continuation of notes from 2/5/08)

there would be 2 electrons in the same state. Also, it
does not matter which electron is given spin up or down, so
(m₁, m₂, mₛ₁, mₛ₂) = (1 1+½ -½) and (1 1 -½ +½) are the
same state. In rows 2, 3, 4, 5 all with mₑ₁ = 1, mₑ₂ = 0, the
two mₑ values are distinct, so there is no restriction on the
mₛ values, which run over all 4 combinations of ±½. The
total number of states is 15, as expected.

The 15-dim space spanned by the states \(|mₗ, mₛ\rangle\)
is invariant under orbital rotations generated by \(\hat{L}\) and
spin rotations generated by \(\hat{S}'\), so it must be possible to
decompose it into invariant, irreducible subspaces characterized
by \(L, S\). Each \(L, S\) value occurs with some
multiplicity; if the multiplicity is >1, we need another index
(\(γ\) above) to resolve the degeneracies. In fact, for light atoms,
the largest multiplicity is 1, and \(γ\) is not needed; the first
atom for which multiplicity >1 occurs is vanadium V.

Now get the allowed \(L, S\) values from the table above. First
look at the state with \(Mₗ=2, Mₛ=0\). This must be the doubly
stretched state of a multiplet with \(L=2, S=0\) (\(^2D\)). First,
since it is the only state with \(Mₗ=2, Mₛ=0\), it is a
nondegen. eigenstate of \( L_z, S_z \). But these commute with \( L^2, S^2 \), so it must be also an eigenstate of them, too. But with what eigenvalues? It cannot be \( L < 2 \), because that would violate the rule \( M_L \leq L \). And it cannot be \( L > 2 \), e.g., \( L = 3 \), because then we would see states with \( M_L = 3 \), and we do not. So it must be \( L = 2 \). Similarly, we conclude \( S = 0 \). So \( |m\text{-set}\rangle \#1 \) in the table is also the state

\[
|LM_L S M_S\rangle = |2 2 00\rangle.
\]

By applying lowering operators, we generate states with \( L = 2, M_L = 2, 1, 0, -1, -2 \) (and \( S, M_S = 0, 0 \)). Take the case

\[
|LM_L S M_S\rangle = |2 1 00\rangle
\]

which has \( M_L = 1, M_S = 0 \). There are 2 \( m\)-sets in the table (row 3,4) with \( M_L = 1, M_S = 0 \), spanning a 2D space, and the one with \( |LM_L S M_S\rangle = |2 1 00\rangle \) is one vector in this space. The vector \( |LM_L S M_S\rangle \) must be the \( \text{stretched} \). Similarly, there are 3 \( m\)-sets with \( M_L = 0, M_S = 0 \) (row 7,8,10) and \( |LM_L S M_S\rangle = |2 0 00\rangle \) must be one vector in this 3D subspace.

Let's list the different \( M_L, M_S \) subspaces and their dimensions, with one check for each state generated by lowering the doubly stretched state

\[
|LM_L S M_S\rangle = |2 2 00\rangle; \quad (4D).
\]
<table>
<thead>
<tr>
<th>$M_L$</th>
<th>$M_S$</th>
<th>dim</th>
<th>$^1D$</th>
<th>$^3P$</th>
<th>$^1S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0</td>
<td>1</td>
<td>✓</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>2</td>
<td></td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>1</td>
<td>-1</td>
<td>1</td>
<td></td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
<td></td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>3</td>
<td></td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>0</td>
<td>-1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-1</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>-1</td>
<td>0</td>
<td>2</td>
<td></td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-2</td>
<td>0</td>
<td>1</td>
<td></td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Now the state with $M_L=1$, $M_S=1$ must also be an eigenstate of $L^2 S^2$ with $L=1$, $S=1$ (a $^3P$ state). It is a doubly stretched state that generates 9 states total when we apply $L_-$ or $S_-$. Finally, the 3rd vector in the $M_L=0$, $M_S=0$ subspace must be an eigenvector of $L^2 S^2$ with $L=0$, $S=0$ (a $^1S$ state). Thus all 15 dim's are accounted for, and we get the same multiplets $^1D$, $^3P$, $^1S$ as before.

Notice that for determining which multiplets occur, we do not need to list any state with $M_L<0$ or $M_S<0$, since
we are identifying multiplets by their doubly stretched members, that always have \( M_L \geq 0 \) and \( M_S \geq 0 \). This simplifies the table. For example, in the case of \( N \) (nitrogen, \( 1s^2 2s^2 2p^3 \)), the table is

<table>
<thead>
<tr>
<th>( n )</th>
<th>( M_L )</th>
<th>( M_{e1} )</th>
<th>( M_{e2} )</th>
<th>( M_{e3} )</th>
<th>( M_S1 )</th>
<th>( M_S2 )</th>
<th>( M_S3 )</th>
<th>( M_L )</th>
<th>( M_S )</th>
<th>( L )</th>
<th>( S )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>( \frac{1}{2} )</td>
<td>2</td>
<td>( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>2</td>
<td>2D</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>( \frac{1}{2} )</td>
<td>( \Omega )</td>
<td>( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>1</td>
<td>2P</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>( \frac{1}{2} )</td>
<td>( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>1</td>
<td>( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>0</td>
<td>3S</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>0</td>
<td>-1</td>
<td>( \frac{1}{2} )</td>
<td>( \frac{1}{2} )</td>
<td>( \frac{1}{2} )</td>
<td>0</td>
<td>( \frac{3}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>0</td>
<td>4S</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>0</td>
<td>-1</td>
<td>( \frac{1}{2} )</td>
<td>( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>0</td>
<td>( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>0</td>
<td>4S</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>0</td>
<td>-1</td>
<td>( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>( \frac{1}{2} )</td>
<td>0</td>
<td>( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>0</td>
<td>4S</td>
</tr>
</tbody>
</table>

Note: State with all 3 \( M_S \)'s equal, \((M_{e1}, M_{e2}, M_{e3}) = (1, 1, 1)\) or \((0, 0, 0)\) impossible, because you can't make the spin states distinct. So we start with \((M_{e1}, M_{e2}, M_{e3}) = (1, 0, 0)\).

In this state, \( M_{S1}, M_{S2} \) must be opposite since \( M_{e1} = M_{e2} \), but \( M_{S3} \) can be anything \( (\pm \frac{1}{2}) \). However, we do not list the state with \( M_{S3} = -\frac{1}{2} \), because it has \( M_S < 0 \). When all 3 \( M_S \)'s are distinct \( (e.g. 1, 0, -1) \), then there are \( 8 = 2^3 \) possibilities for \( M_S \), but we only have 4 with \( M_S > 0 \) \( (e.g. \) rows \((3, 4, 5, 6)\). By looking for doubly stretched states we find the multiplets \( ^2D, ^2P, ^4S \) with dimensions \( 2 \times 5 = 10, 2 \times 3 = 6, 4 \times 1 = 4 \), \( 10 + 6 + 4 = 20 = \binom{6}{3} \).
Continuing atomic structure...

Next case is O (oxygen) with config \(1s^2 2s^2 2p^4\). But it turns out that holes behave same way as electrons, insofar as computing allowed multiplets is concerned. The \(2p\) subshell has 6 slots; when we add 4 electrons, there remain 2 empty slots, or "holes". These behave like electrons for computing multiplets since a completely empty subshell and a completely full one both have \(L=M_L=S=M_S=0\). Thus O (oxygen) has same multiplets as carbon. Now it is easy to list the multiplets of the ground state configurations of the first several elements:

<table>
<thead>
<tr>
<th>Z</th>
<th>element</th>
<th>config</th>
<th>multiplets</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>1s</td>
<td>2S</td>
</tr>
<tr>
<td>2</td>
<td>He</td>
<td>1s^2</td>
<td>1S</td>
</tr>
<tr>
<td>3</td>
<td>Li</td>
<td>1s^2 2s</td>
<td>2S</td>
</tr>
<tr>
<td>4</td>
<td>Be</td>
<td>1s^2 2s^2</td>
<td>1S</td>
</tr>
<tr>
<td>5</td>
<td>B</td>
<td>1s^2 2s^2 2p</td>
<td>2P</td>
</tr>
<tr>
<td>6</td>
<td>C</td>
<td>1s^2 2s^2 2p^2</td>
<td>3P, 1D, 1S</td>
</tr>
<tr>
<td>7</td>
<td>N</td>
<td>1s^2 2s^2 2p^3</td>
<td>4S, 2D, 2P</td>
</tr>
<tr>
<td>8</td>
<td>O</td>
<td>1s^2 2s^2 2p^4</td>
<td>3P, 1D, 1S</td>
</tr>
<tr>
<td>9</td>
<td>F</td>
<td>1s^2 2s^2 2p^5</td>
<td>2P</td>
</tr>
<tr>
<td>10</td>
<td>Ne</td>
<td>1s^2 2s^2 2p^6</td>
<td>1S</td>
</tr>
</tbody>
</table>

When we go to heavier elements (more complicated configurations), it is possible that some multiplets occur more than once. This first happens with V (vanadium). In these cases there is more than one way to create multiplets of given \(L, S\), and we need an extra
index, say, \( \gamma \), in the specification of the unperturbed eigenstates:

\[
| \gamma L M_l S M_s \rangle = \sum_{m\text{-sets}} (\text{coefs}) | m\text{-sets} \rangle
\]

 stil understood that we are working within a given configuration).

These calculations of allowed multiplets just tell us which \( L, S \) values occur in the given configuration of \( H_0 \). To do perturbation theory with \( H_1 \), we also need the coeffs in the expansion above. These are generalizations of the C-G coeffs and can be found with raising and lowering operators. Once that is done, we can do perturbation theory with \( H_1 \).

We need to find the eigenvalues of

\[
\langle \gamma' L M_l S M_s | H_1 | \gamma L M_l S M_s \rangle
\]

No primes are needed on \( L, M_l, S, M_s \) on the right because \( L^2, Lz, S^2, Sz \) all commute with \( H_1 \). In cases like C or N, where no multiplet occurs more than once, we don't need the \( \gamma \) indices, and the energy shifts are just the diagonal elements of \( H_1 \). Evaluating these matrix elements would take us too far afield, but when you do it, some rules emerge about the energy shifts. Notice that the energy shifts due to \( H_1 \) depend on \( L \) and \( S \), (i.e., which multiplet) but not on \( M_l, M_s \) (because of WE then).

The following rules (semi-empirical) govern the ordering of the
energy shifts. (Hund's rules:)

1. The lowest multiplet has the highest S
2. For given S, the lowest multiplet has the highest L.

The physics of rule #1 is familiar: higher S means more symmetric spin states, which means more anti-symmetric spatial states, which means lower Coulomb energy. This is what made the triplet states lower in energy than the singlet states in helium, and it also lies behind ferromagnetism (align spins, lower Coulomb energy). We won't try to justify rule 2 physically.

These rules allow us to order the multiplets in C and N:

\[ 1s^2 2s^2 2p^2 \text{ (15)} \]
\[ 1s^2 2s^2 2p^3 \text{ (20)} \]
Now consider $H_2$ (the spin-orbit term). This term itself is an approximation, since it pretends that each electron moves in a central force potential. Even in the $HF$ appx, this neglects the exchange (nonlocal) potential. We will just summarize some results.

First, $H_2$ does not commute with $\mathbf{L}$ or $\mathbf{S}$, but with $\mathbf{J} = \mathbf{L} + \mathbf{S}$. So we couple $\mathbf{L} + \mathbf{S}$ to get eigenbasis of $J^0, J_z$:

$$|y LSJM>G = \sum_{M,L,M_S} |y LSJM_S M_S > \langle LS M_L M_S | J^0 M_J \rangle$$

just like in Hydrogen. Then one can show

$$\langle LSJM | \sum_i \xi^{(r;)} \mathbf{L}_i \cdot \mathbf{S}_i | LSJM_G \rangle$$

$$= A \langle LSJM | \mathbf{L} \cdot \mathbf{S} | LSJM_G \rangle$$

$$= \frac{A}{2} [ J(J+1) - L(L+1) - S(S+1) ].$$

So energy is $\uparrow$ for $J$ if $A > 0$, $\downarrow$ for $J$ if $A < 0$. In fact,

- $\frac{1}{2}$ filled subshells $A > 0$ ("regular" multiplet)
- $\frac{1}{2}$ filled subshells $A < 0$ ("inverted" multiplet)
- $\frac{1}{2}$ filled $A = 0$ (must go on to 2nd order past $H_0$).
With \( J \) values, levels of \( C, N, O \) are:

\[
\begin{align*}
\text{C} & : 1s^2 2s^2 2p^2 \\
\begin{array}{c}
\text{4s} \\
\text{4d} \\
\text{3p}
\end{array} & \left\{ \begin{array}{c}
\text{4s}_0 \\
\text{4d}_2 \\
\text{3p}_2, \text{3p}_1, \text{3p}_0
\end{array} \right\} \text{ regular fine structure multiplet}
\end{align*}
\]

\[
\begin{align*}
\text{H}_0 + \text{H}_1 & \quad \text{H}_0 + \text{H}_1 + \text{H}_2
\end{align*}
\]

\[
\begin{align*}
\text{N} & : 1s^2 2s^2 2p^3 \\
\begin{array}{c}
\text{2p} \\
\text{2d}
\end{array} & \left\{ \begin{array}{c}
\text{3p}_2, \text{3p}_1 \\
\text{2d}_3, \text{2d}_5
\end{array} \right\} \text{ fine structure}
\end{align*}
\]

\[
\begin{align*}
\text{H}_0 + \text{H}_1 & \quad \text{H}_0 + \text{H}_1 + \text{H}_2
\end{align*}
\]

\[
\begin{align*}
\text{O} & : 1s^2 2s^2 2p^4 \\
\begin{array}{c}
\text{1s} \\
\text{1d}
\end{array} & \left\{ \begin{array}{c}
\text{4s}_0 \\
\text{4d}_2
\end{array} \right\} \text{ inverted multiplet}
\end{align*}
\]

\[
\begin{align*}
\text{3p}_2, \text{3p}_1, \text{3p}_0
\end{align*}
\]

Subscript is \( J \)-value, e.g. \( ^3\text{P}_2 \) means \( S=1, L=1, J=2 \).

Diagrams not to scale, in particular, fine structure splitting \( \ll \) splitting between multiplets, which is on order of \( \sim 10^{-2} \) 1-3 ev. or so.